



Rare Earth and Actinide Complexes

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The rare earth metals (scandium, yttrium, lanthanum and the subsequent 4f elements) and actinides (actinium and the 5f elements) are vital components of our technology-dominated society. Examples include the fluorescent-red europium ions used in euro banknotes to deter counterfeiting [1], the radioactive americium used in smoke detectors [2] that save countless lives every year as well as neodymium used in the strongest permanent magnets [3]. However, the rare earth and actinide elements remain poorly recognised by non-scientists, and even by many undergraduates in chemistry.

The similar radii of the respective +3 cations (Figure 1) belies their individually unique spectral [4] and magnetic [5] properties that contribute to their fascinating chemistry. In this Special Issue, devoted to molecular rare earth and actinide complexes, work from Natrajan and co-workers [6] has explored how fluorinated ligands improve the luminescence of 4f complexes, while Baker and co-workers [7] investigated the optical properties, as well as structure, of a new class of uranyl selenocyanate. Pointillart and co-workers' article [8] bridges the areas of lanthanide optical and magnetic properties—literally—by using bridging tetrathiafulvalene derivatives. The growing field of Single Molecule Magnetism originates in the d-block, but recent interest in the f-elements has been growing. Powell and co-workers [9] explore the use of dimeric dysprosium (which has a highly anisotropic f-electron distribution) compounds with a “hula-hoop” geometry, defined by the ligand that sits in an equatorial plane around both Dy atoms. The main current medical use for the lanthanides, as Magnetic Resonance Imaging (MRI) contrast agents, also relies on the unique electronic properties of the lanthanides. The article by Parac-Vogt and co-workers [10] demonstrates the combination of gadolinium for MRI imaging (thanks to its seven unpaired electrons) connected to a luminescent BODIPY fragment in order to explore combined MRI and optical imaging, addressing the drawbacks of both techniques through their complementary properties.

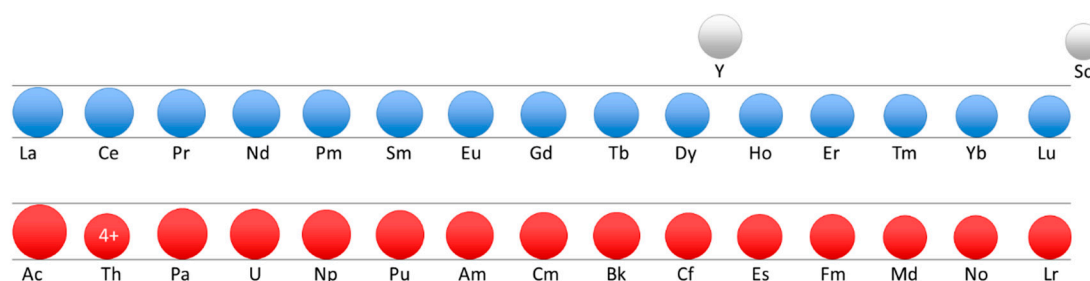


Figure 1. The ionic radii of the 6-coordinate M^{3+} cations of the rare earth and actinide metals (except for Th which is Th^{4+}) [11–13].

Another growing application of molecular lanthanide complexes is in catalysis, and in this issue, Kostakis and co-workers [14] report the use of lanthanide coordination polymers as catalysts in

a domino reaction. As with the d-block, organometallic lanthanide chemistry has proven to be of vital use in the development of homogeneous catalysis. This issue reflects this growing interest with papers demonstrating the synthesis of organometallic lanthanide complexes using imide (Anwander and co-workers) [15], amidinate (Edelman and co-workers) [16], reduced bipyridine (Mills and co-workers) [17] and metallocene (Ce^{4+} complexes by Gordon and co-workers [18], the reactivity of Sm^{2+} by Maron and co-workers [19] and $\text{U}^{3+}/\text{U}^{4+}$ bromides by Kiplinger and co-workers [20]) ligand frameworks. A review from Eisen and co-workers [21] is devoted to actinide catalysis and an article from Visseaux and co-workers [22] details the extension of organometallic Nd catalysis into the solid state demonstrating the numerous current applications of these interesting species. The review by Turner [23] highlights N_2 and P_4 activation chemistry of the f-block, an area of great future catalytic potential.

We hope you will enjoy the breadth of chemistry offered in this open access Special Issue that highlights the many differences between complexes of the rare earths and actinides. However, the similarity of ionic radii is inescapable for the +3 oxidation state, which gives rise to one of the most challenging remaining problems for f-block chemists and the potential renaissance of nuclear power (as well as tackling historical problems). The separation of highly radioactive and frustratingly long-lived heavier actinides from shorter-lived radioactive isotopes of the lanthanides would greatly aid planning for the long-term storage of nuclear waste. It is promising that the current resurgence of interest in the fundamental chemistry of the f-block can feed into the goal of discriminating between the actinides and lanthanides based on differences in bonding and reactivity thereby boosting efforts in the area of nuclear waste separation and storage. In fact, the article by Beekmeyer and Kerridge compares covalency in $[\text{CeCl}_6]^{n-}$ and $[\text{UCl}_6]^{n-}$ as a means of shedding light on this very problem [24]. We look forward to many more academic and practical advances in all of the above fields of research in the near future.

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